

FLAME RETARDANT CARBONATE POLYMER COMPOSITION

FIELD OF THE INVENTION

This invention relates to a flame retardant carbonate polymer.

BACKGROUND OF THE INVENTION

The use of organophosphorus flame retardants for imparting fire-retarding properties to thermoplastic resins is known. For example, U.S. Patent No. 5,204,394 discloses thermoplastic resin compositions that contain an aromatic polycarbonate resin, a styrene-containing graft copolymer and an oligomeric organophosphorus flame retardant.

A thermoplastic resin composition that exhibits good flame retardant properties and that maintains an overall balance of physical properties under hydrolytic conditions is desired.

SUMMARY OF THE INVENTION

In a first embodiment, the present invention is directed to a thermoplastic resin composition, comprising:

- (a) one or more thermoplastic resins, comprising at least one aromatic carbonate resin,
- (b) a flame-retarding amount of an organophosphorus flame retardant compound, and
- (c) a flame retarding amount of a polyimide compound.

In a second embodiment, the present invention is directed to a process for making a flame retardant thermoplastic resin composition, comprising combining a thermoplastic resin, said resin comprising at least one aromatic

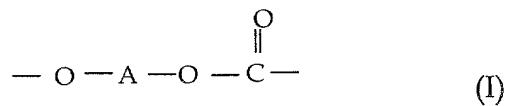
polycarbonate resin, a flame-retarding amount of a organophosphorus flame retardant compound and a flame retarding amount of a polyimide compound as described above.

DETAILED DESCRIPTION OF THE INVENTION

In preferred embodiments, the composition of the present invention comprises from 50 to 95 parts by weight ("pbw"), or from 55 to 95 pbw or from 60 to 90 pbw, of the thermoplastic resin which may comprise one or more thermoplastic polymers or resins, from 0 to 15 pbw, or from 1 to 15 pbw and or preferably from 2 to 10 pbw, of the organophosphorus compound, from 0.10 to 20 pbw, or from 0.50 to 15 pbw or from 1 to 10 pbw, of the polyimide compound each based on 100 pbw of the combined amount of thermoplastic resin, organophosphorus and polyimide compound.

Suitable aromatic carbonate resins include aromatic polycarbonate resins and aromatic copolyester-carbonate resins.

Aromatic polycarbonate resins are known compounds and the properties and methods of making polycarbonate resins are also known. Typically these are prepared by reacting a dihydric phenol with a carbonate precursor, such as phosgene, a haloformate or a carbonate ester and generally in the presence of an acid acceptor and a molecular weight regulator. Generally speaking, such carbonate polymers may be typified as possessing recurring structural units of the formula (I):



wherein A is a divalent aromatic radical of the dihydric phenol employed in the polymer reaction. The dihydric phenol which may be employed to provide such aromatic carbonate polymers are mononuclear or polynuclear aromatic

compounds, containing as functional groups two hydroxy radicals, each of which maybe attached directly to a carbon atom of an aromatic nucleus.

Typical dihydric phenols are: 2,2-bis(4-hydroxyphenyl) propane; hydroquinone; resorcinol; 2,2-bis(4-hydroxyphenyl) pentane; 2,4'- (dihydroxydiphenyl) methane; bis(2-hydroxyphenyl) methane; bis(4-hydroxyphenyl) methane; 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane; fluorenone bisphenol, 1,1-bis(4-hydroxyphenyl) ethane; 3,3-bis(4-hydroxyphenyl) pentane; 2,2'-dihydroxydiphenyl; 2,6-dihydroxynaphthalene; bis(4-hydroxydiphenyl)sulfone; bis(3,5-diethyl-4-hydroxyphenyl)sulfone; 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane; 2,2-bis(3,5-dimethoxyphenyl)propane; 2,4'-dihydroxydiphenyl sulfone; 5'-chloro-2,4'-dihydroxydiphenyl sulfone; 4,4'-dihydroxydiphenyl ether; 4,4'-dihydroxy-3,3'-dichlorodiphenyl ether, spiro biindane bis phenol, and the like.

These aromatic polycarbonates can be manufactured by known processes, such as, for example and as mentioned above, by reacting a dihydric phenol with a carbonate precursor, such as phosgene, in accordance with methods set forth in the literature including the melt polymerization process. Generally in the melt polymerization process, a diphenyl carbonate is reacted with a bisphenol.

The carbonate precursor employed in preparing the polycarbonate of this invention can be either carbonyl halide or a haloformate. The carbonyl halides which can be employed herein are, for example carbonyl bromide, carbonyl chloride, etc.; or mixtures thereof. The haloformates suitable for use herein include bishaloformates of dihydric phenols (bischloroformates of bis phenol A, hydroquinone, etc.) or glycols (bishaloformates of ethylene glycol, neopentyl glycol, polyethylene glycol, etc.). While other carbonate precursors will occur to those skilled in the art, carbonyl chloride, also known as phosgene is preferred.

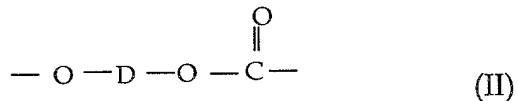
The reaction disclosed above is preferably known as an interfacial reaction between the dihydric compound and a carbonyl chloride such as phosgene. Another process for preparing the aromatic polycarbonate employed in this invention is the transesterification process which involves the transesterification of an aromatic dihydroxy compound and a diester carbonate. This process is known as the melt polymerization process. In the practice of this invention, the process of producing the aromatic polycarbonate is not critical. As used herein, aromatic carbonate polymer shall mean and include any of the aromatic polycarbonates, blends thereof with other polymer, copolymers thereof, copolyester carbonates, and mixtures thereof.

It is also possible to employ two or more different dihydric phenols or a copolymer of a dihydric phenol with a glycol or with a hydroxy- or acid-terminated polyester or with a dibasic acid or hydroxy acid in the event a carbonate copolymer or interpolymer rather than a homopolymer is desired for use in the preparation of the polycarbonate mixtures of the invention. Polyarylates and polyester-carbonate resins or their blends can also be employed. Branched polycarbonates are also useful and are well disclosed in the literature. Also, blends of linear polycarbonate and a branched polycarbonate can be utilized herein. Moreover, blends of any of the above materials may be employed in the practice of this invention to provide the aromatic polycarbonate component of the carbonate polymer composition.

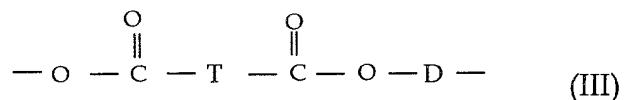
In any event, the preferred aromatic polycarbonate for use in the practice in the present invention is a homopolymer, for example, a homopolymer derived from 2,2-bis(4-hydroxyphenyl)propane (bisphenol-A) and phosgene, commercially available.

The aromatic carbonate polymers also suitable for use in this invention include polyester-carbonates, also known as copolyester-polycarbonates, that is,

resins which contain, in addition to recurring polycarbonate chain units of the formula (II):



wherein D is a divalent aromatic radical of the dihydric phenol employed in the polymerization reaction, repeating or recurring carboxylate units, for example of the formula (III):



wherein D is a defined above and T is an aromatic radical such as phenylene, naphthylene, biphenylene, substituted phenylene and the like; a divalent aliphatic-aromatic hydrocarbon radical such as an alkaryl or alkaryl radical; or two or more aromatic groups connected through such aromatic linkages which are known in the art.

The copolyester-polycarbonate resins are also prepared by interfacial polymerization technique, well known to those skilled in the art (see for example U.S. Patent 3,169,121 and 4,487,896).

In general, any dicarboxylic acid conventionally used in the preparation of linear polyesters may be utilized in the preparation of the copolyester carbonate resins of the instant invention. Generally, the dicarboxylic acids which may be utilized include the aliphatic dicarboxylic acids, the aromatic dicarboxylic acids, and the aliphatic-aromatic dicarboxylic acids. These acids are well known and are disclosed for example in U.S. Patent 3,169,121 which is hereby incorporated herein by reference. Mixtures of dicarboxylic acids may be employed. Therefore, where the term dicarboxylic acid is used herein it is to be understood that this term includes mixtures of two or more dicarboxylic acids.

Most preferred as aromatic dicarboxylic acids are isophthalic acid, terephthalic acids, and mixtures thereof. A particularly useful difunctional carboxylic acid comprises a mixture of isophthalic acid and terephthalic acid wherein the weight ratio of terephthalic acid to isophthalic acid is in the range of from about 10:1 to about 0.2:9:8.

Rather than utilizing the dicarboxylic acid per se, it is possible, and sometimes even preferred, to employ the reactive derivatives of said acid. Illustrative of these reactive derivatives are the acid halides. The preferred acid halides are the acid dichlorides and the acid dibromides. Thus, for example instead of using isophthalic acid, terephthalic acid or mixtures thereof, it is possible to employ isophthaloyl dichloride, terephthaloyl dichloride, and mixtures thereof.

The aromatic polycarbonate resins may be linear or branched and, generally, will have a weight average molecular weight of from about 10,000 to about 200,000 grams per mole ("g/mol"), preferably from about 20,000 to about 100,000 g/mol, as measured by gel permeation chromatography. Such resins typically exhibit an intrinsic viscosity, as determined in chloroform at 25°C of from about 0.3 to about 1.5 deciliters per gram (dl/gm), preferably from about 0.45 to about 1.0 dl/gm.

The branched polycarbonates may be prepared by adding a branching agent during polymerization. These branching agents are well known and may comprise polyfunctional organic compounds containing at least three functional groups which may be hydroxyl, carboxyl, carboxylic anhydride, haloformyl and mixtures thereof. Specific examples include trimellitic acid, trimellitic anhydride, trimellitic trichloride, tris-p-hydroxy phenyl ethane, isatin-bis-phenol, tris-phenol TC (1,3,5-tris((p-hydroxyphenyl)isopropyl)benzene), tris-phenol PA (4(4(1,1-bis(p-hydroxyphenyl)-ethyl)alpha, alpha-dimethyl benzyl)phenol), 4-chloroformyl

phthalic anhydride, trimesic acid and benzophenone tetracarboxylic acid. The branching agent may be added at a level of about 0.05-2.0 weight percent.

All types of polycarbonates end groups are contemplated as being within the scope of the present invention with respect to the polycarbonate component of a carbonate polymer composition.

The thermoplastic resin component of the composition of the present invention may, optionally, further comprise one or more other thermoplastic resins in addition to the aromatic carbonate resin, such as, for example, polyphenylene ether resins, vinyl aromatic graft copolymers resins, styrenic resins, polyester resins, polyamide resins, polyesteramide resins, and polysulfone resins.

In a preferred embodiment, the composition of the present invention comprises an aromatic polycarbonate resin and a vinyl aromatic graft copolymer.

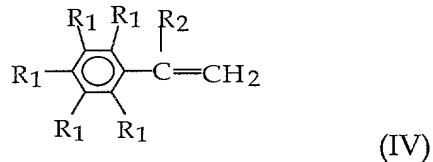
In a preferred embodiment, the thermoplastic resin component of the composition of the present invention comprises, based on 100 pbw of the thermoplastic resin component, from 30 to 95 pbw, more preferably from 50 to 95 pbw, still more preferably from 60 to 90 pbw of an aromatic polycarbonate resin and from 1 to 70 pbw, more preferably from 50 to 95 pbw, still more preferably from 10 to 40 pbw of a vinyl aromatic graft copolymer.

Suitable vinyl aromatic graft copolymers comprise (i) a rubber modified monovinylidene aromatic graft copolymer component and (ii) an ungrafted rigid copolymer component, and are generally prepared by graft polymerization of a mixture of a monovinylidene aromatic monomer and one or more comonomers in the presence of one or more rubbery polymeric substrates. Depending on the amount of rubber present, a separate matrix or continuous rigid phase of ungrafted rigid (co)polymer may be simultaneously

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obtained along with the rubber modified monovinylidene aromatic graft polymer. The resins may also be produced by blending a rigid monovinylidene aromatic copolymer with one or more rubber modified monovinylidene aromatic graft copolymers. Typically, the rubber modified resins comprise the rubber modified graft copolymer at a level of from 5 to 100 percent by weight ("wt%") based on the total weight of the resin, preferably from 10 to 90 wt% thereof, and more preferably 30 to 80 wt% thereof. The rubber modified resin comprises the ungrafted rigid polymer at a level of from 95 to 0 wt% based on the total weight of the resin, preferably from 90 to 10 wt% thereof, and more preferably from 70 to 20 wt% thereof.

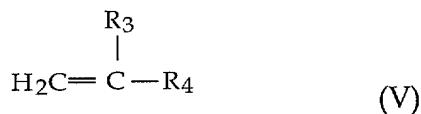
Monovinylidene aromatic monomers which may be employed include styrene, -methyl styrene, halostyrenes, that is, dibromostyrene, mono or di alkyl, alkoxy or hydroxy substitute groups on the nuclear ring of the monovinylidene aromatic monomer, that is, vinyl toluene, vinylxylene, butylstyrene, parahydroxystyrene or methoxystyrene or mixtures thereof. The monovinylidene aromatic monomers utilized are generically described by the following formula (IV):



wherein each R₁ is independently H, (C₁-C₆)alkyl, cycloalkyl, aryl; alkaryl, aralkyl, alkoxy, aryloxy, or halo, such as, for example, such as bromine and chlorine, and R₂ is selected from the group consisting of H, (C₁-C₆)alkyl and halo. As used herein, the notation "(C_x-C_y)" in reference to an organic moiety means that the organic moiety contains from x carbons to y carbons. Examples of substituted vinylaromatic compounds include styrene, 4-methylstyrene, 3,5-diethylstyrene, 4-n-propylstyrene, -methylstyrene, -methyl vinyltoluene, -

chlorostyrene, -bromostyrene, dichlorostyrene, dibromostyrene, tetrachlorostyrene, mixtures thereof and the like. The preferred monovinylidene aromatic monomers used are styrene and/or -methylstyrene.

Comonomers which may be used with the monovinylidene aromatic monomer includes acrylonitrile, methacrylonitrile, (C₁-C₈)alkyl or aryl substituted acrylate, (C₁-C₈)alkyl, aryl or haloaryl substituted methacrylate, acrylic acid, methacrylic acid, itaconic acid, acrylamide, N-substituted acrylamide or methacrylamide, maleic anhydride, maleimide, N-alkyl, aryl or haloaryl substituted maleimide, glycidyl (meth)acrylates, hydroxy alkyl (meth)acrylates or mixtures thereof. The acrylonitrile, substituted acrylonitrile, or acrylic acid esters are described generically by the following formula (V):



wherein R₃ is H or C₁-C₆)alkyl and R₄ is selected from the group consisting of cyano and (C₁-C₁₆)alkoxycarbonyl. Examples of such monomers include acrylonitrile, ethacrylonitrile, methacrylonitrile, -chloroacrylonitrile, -bromoacrylonitrile, methyl acrylate, methyl methacrylate, ethyl acrylate, butyl acrylate, propyl acrylate, isopropyl acrylate and mixtures thereof. The preferred monomer is acrylonitrile and the preferred acrylic acid esters are ethyl acrylate and methyl methacrylate. It is also preferred that the acrylic acid esters, when included, are employed in combination with styrene or acrylonitrile.

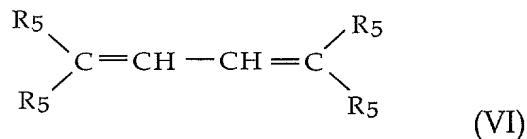
The rubber modified graft copolymer preferably comprises (i) the rubber substrate, and (ii) a rigid polymeric superstrate portion grafted to the rubber substrate. The rubber substrate is preferably present in the graft copolymer at a level of from 5 to 80 wt% based on the total weight of the graft copolymer, more preferably from 10 to 70 wt% thereof. The rigid superstrate is preferably

present at a level of from 95 to 20 wt% based on the total weight of the graft copolymer, and more preferably from 90 to 30 wt% thereof.

Examples of rubbery polymers for the substrate include: conjugated dienes, copolymers of a diene with styrene, acrylonitrile, methacrylonitrile or (C_1 - C_8)alkyl acrylate which contain at least 50% (preferably at least 65% by weight) conjugated dienes, polyisoprene or mixtures thereof; olefin rubbers, that is, ethylene propylene copolymers (EPR) or ethylene propylene non-conjugated diene copolymers (EPDM); silicone rubbers; or (C_1 - C_8)alkyl acrylate homopolymers or copolymers with butadiene and/or styrene. The acrylic polymer may also contain up to 5% of one or more polyfunctional crosslinking agents such as alkylenediol di(meth)acrylates, alkylenetriol tri (meth) acrylates, polyester di(meth)acrylates, divinylbenzene, trivinylbenzene, butadiene, isoprene and optionally graftable monomers such as, triallyl cyanurate, triallyl isocyanurate, allyl (meth)acrylate, diallyl maleate, diallyl fumarate, diallyl adipate, triallyl esters of citric acid or mixtures of these agents.

The diene rubbers may preferably be polybutadiene, polyisoprene and copolymers of butadiene with up to 35% by weight of (C_1 - C_8)alkylacrylate which are produced by aqueous radical emulsion polymerization. The acrylate rubbers may be cross-linked, particulate emulsion copolymers substantially of (C_1 - C_8)alkylacrylate, in particular (C_1 - C_6)alkylacrylate, optionally in admixture with up to 15% by weight of comonomers such as styrene, methylmethacrylate, butadiene, vinyl methyl ether or acrylonitrile and optionally up to 5% by weight of a polyfunctional crosslinking comonomer, for example, divinylbenzene, glycolbis-acrylates, bisacrylamides, phosphoric acid triallylester, citric acid triallyl-ester, allylesters or acrylic acid or methacrylic acid, triallylcyanurate, triallylisocyanurate. Also suitable are mixtures of diene- and alkylacrylate rubbers and rubbers which have a so-called core/shell structure, for example, a core of diene rubber and a shell of acrylate or vice versa.

Specific conjugated diene monomers normally utilized in preparing the rubber substrate of the graft polymer are generically described by the following formula (VI):



wherein each R₅ is independently H, (C₁-C₆)alkyl, chlorine or bromine.

Examples of dienes that may be used are butadiene, isoprene, 1,3-heptadiene, methyl-1,3-pentadiene, 2,3-dimethylbutadiene, 2-ethyl-1,3-pentadiene 1,3- and 2,4-hexadienes, chloro and bromo substituted butadienes such as dichlorobutadiene, bromobutadiene, dibromobutadiene, mixtures thereof, and the like. A preferred conjugated diene is 1,3 butadiene.

The substrate polymer, as mentioned, is preferably a conjugated diene polymer such as polybutadiene, polyisoprene, or a copolymer, such as butadiene-styrene, butadiene-acrylonitrile, or the like. The rubbery polymeric substrate portion must exhibit a glass transition temperature (T_g) of less than about 0°C.

Mixtures of one or more rubbery polymers previously described for preparing the monovinylidene aromatic graft polymers, or mixtures of one or more rubber modified monovinylidene aromatic graft polymers disclosed herein may also be employed. Furthermore, the rubber may comprise either a block or random copolymer. The rubber particle size used in this invention as measured by simple light transmission methods or capillary hydrodynamic chromatography (CHDF) may be described as having an average particle size by weight of 0.05 to 1.2 microns, preferably 0.2 to 0.8 microns, for emulsion based polymerized rubber latices or 0.5 to 10 microns, preferably 0.6 to 1.5 microns, for mass polymerized rubber substrates which also have included

grafted monomer occlusions. The rubber substrate is preferably a particulate, moderately cross-linked diene or alkyl acrylate rubber, and preferably has a gel content greater than 70%.

Preferred graft superstrates include copolymers of styrene and acrylonitrile, copolymers of α -methylstyrene and acrylonitrile and methylmethacrylate polymers or copolymers with up to 50% by weight of (C_1-C_6)alkylacrylates, acrylonitrile or styrene. Specific examples of monovinylidene aromatic graft copolymers include but are not limited to the following: acrylonitrile-butadiene-styrene (ABS), acrylonitrile-styrene-butyl acrylate (ASA), methylmethacrylate-acrylonitrile-butadiene styrene (MABS), acrylonitrile-ethylene-propylene-non-conjugated diene-styrene (AES).

The ungrafted rigid polymers (typically free of rubber) are resinous, thermoplastic polymers of styrene, α -methylstyrene, styrenes substituted in the nucleus such as para-methylstyrene, methyl acrylate, methylmethacrylate, acrylonitrile, methacrylonitrile, maleic acid anhydride, N-substituted maleimide, vinyl acetate or mixtures thereof. Styrene/acrylonitrile copolymers, α -methylstyrene/acrylonitrile copolymers and methylmethacrylate/acrylonitrile copolymers are preferred.

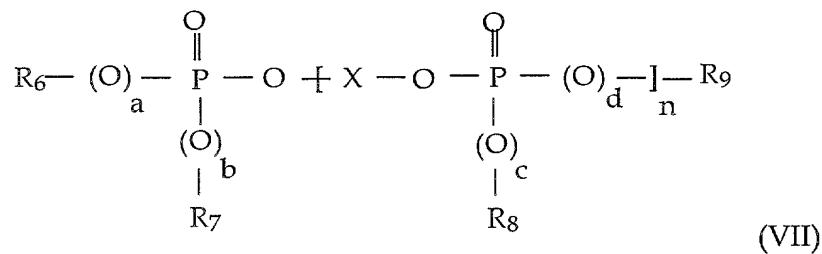
The ungrafted rigid copolymers are known and may be prepared by radical polymerization, in particular by emulsion, suspension, solution or bulk polymerization. They preferably have number average molecular weights of from 20,000 to 200,000 g/mol and limiting viscosity numbers [η] of from 20 to 110 ml/g (determined in dimethylformamide at 25°C).

The number average molecular weight of the grafted rigid superstrate of the monovinylidene aromatic resin is designed to be in the range of 20,000 to 350,000 g/mol. The ratio of monovinylidene aromatic monomer to the second and optionally third monomer may be range from 90/10 to 50/50 preferably

80/20 to 60/40. The third monomer may optional replace 0 to 50 percent of one or both of the first and second monomers.

These rubber modified monovinylidene aromatic graft polymers may be polymerized either by mass, emulsion, suspension, solution or combined processes such as bulk-suspension, emulsion-bulk, bulk-solution or other techniques well known in the art. Furthermore, these rubber modified monovinylidene aromatic graft copolymers may be produced either by continuous, semibatch or batch processes.

In a preferred embodiment, the organophosphorus compound comprises one or more compounds according to the structural formula (VII):



wherein R₆, R₇, R₈ and R₉ are each independently aryl, optionally substituted with halo or (C₁-C₆)alkyl,

X is arylene, optionally substituted with halo or (C₁-C₆)alkyl,

a, b, c and d are each independently 0 or 1, and

n is an integer from 0 to 5, more preferably from 1 to 5.

As used herein, the term "aryl" means a monovalent radical containing one or more aromatic rings per radical, which may optionally be substituted on the one or more aromatic rings with one or more alkyl groups, each preferably (C₁-C₆)alkyl and which, in the case wherein the radical contains two or more rings, may be fused rings.

As used herein, the term "arylene" means a divalent radical containing one or more aromatic rings per radical, which may optionally be substituted on the one or more aromatic rings with one or more alkyl groups, each preferably (C₁-C₆)alkyl and which, in the case wherein the divalent radical contains two or more rings, the rings may be fused or may be joined by a non-aromatic linkages, such as for example, an alkylene, alkylidene, any of which may be substituted at one or more sites on the aromatic ring with a halo group or (C₁-C₆)alkyl group.

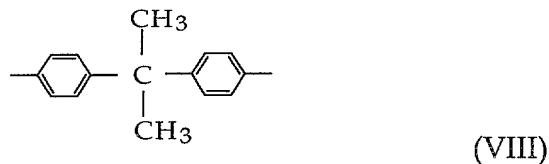
In a preferred embodiment, the organophosphorus compound comprises a blend of organophosphorus compound oligomers according to formula (8), wherein n for each oligomer is an integer of from 1 to 5 and the blend has an average n value of greater than 1 to less than 5, more preferably greater than 1 to less than 3, even more preferably, greater than 1 to less than 2.

In highly preferred embodiment, the organophosphorus compound comprises one or more resorcinol diphosphate ("RDP") esters according to formula (8), wherein R₆, R₇, R₈ and R₉ are each phenyl, a, b, c and d are each 1, X is 1,3-phenylene and n is an integer from 1 to 5.

More preferably, the organophosphorus compound comprises a blend of RDP oligomers, wherein n for each oligomer is an integer of from 1 to 5 and the blend has an average n value of greater than 1 to less than 5, more preferably from greater than 1 to less than 3, even more preferably, from greater than 1 to less than 2.

In a more highly preferred embodiment, the organophosphorus compound comprises one or more bisphenol A diphosphate ("BPA-DP") esters according to formula (8), wherein R₆, R₇, R₈ and R₉ are each phenyl, a,

b, c and d are each 1, and X is a divalent aromatic radical of the structural formula (VIII)):

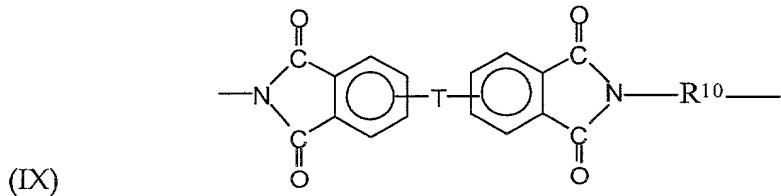


and n is an integer from 1 to 5.

More preferably, the organophosphorus compound comprises a blend of BPA-DP oligomers, wherein n for each oligomer is an integer of from 1 to 5 and the blend has an average n value of greater than 1 to less than 5, more preferably from greater than 1 to less than 3, and even more preferably, from greater than 1 to less than 2.

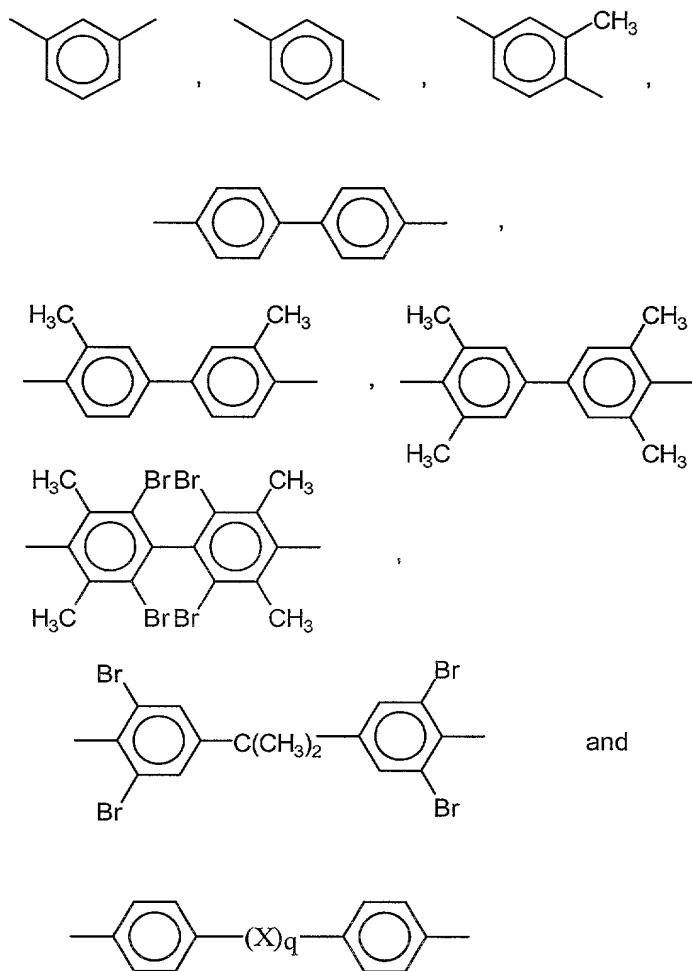
In another preferred embodiment, the organophosphorus compound component of the composition of the present invention comprises a mixture of from about 1 to about 99 wt% of one or more BPA-DP esters and about 1 to about 99 wt% of one or more RDP esters.

In one embodiment, the resin is a polyetherimide resin comprising structural units of the formula (IX):



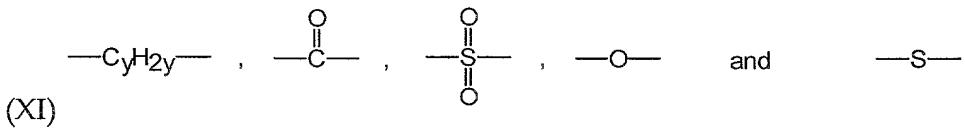
wherein the divalent T moiety bridges the 3,3', 3,4', 4,3', or 4,4' positions of the aryl rings of the respective aryl imide moieties; T is -O- or a group of the

formula -O-Z-O- ; Z is a divalent radical selected from the group consisting of formulae (X):

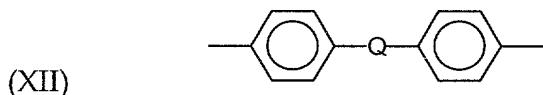


(X)

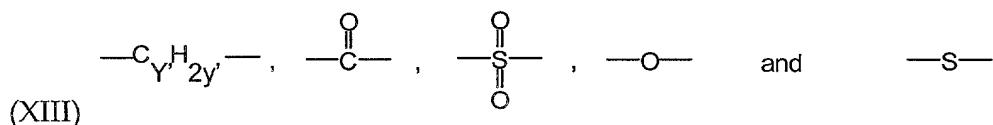
wherein X is a member selected from the group consisting of divalent radicals of the formulae (XI):



wherein y is an integer from 1 to about 5, and q is 0 or 1; R¹⁰ is a divalent organic radical selected from the group consisting of: (a) aromatic hydrocarbon radicals having from 6 to about 20 carbon atoms and halogenated derivatives thereof, (b) alkylene radicals having from 2 to about 20 carbon atoms, (c) cycloalkylene radicals having from 3 to about 20 carbon atoms, and (d) divalent radicals of the general formula (XII):

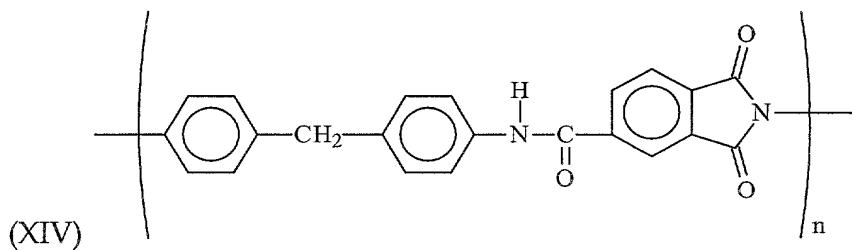


where Q is a member selected from the group consisting of formulae (XIII):

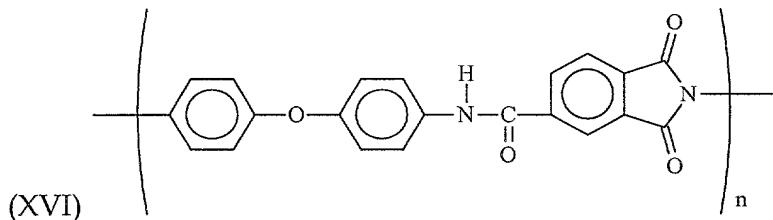
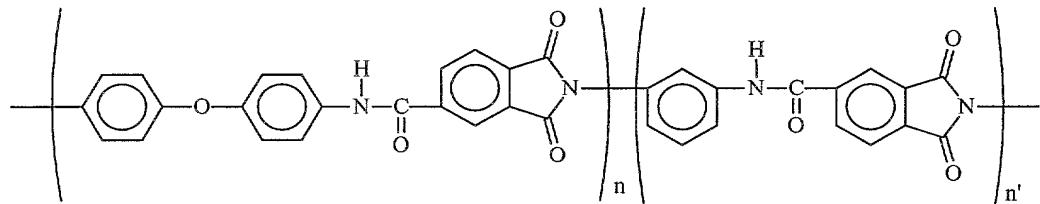


where y' is an integer from about 1 to about 5. A particularly preferred polyetherimide resin is the reaction product formed by melt polymerization of 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride with one or more of paraphenylene diamine and metaphenylene diamine. The resins are commercially available from GE Plastics under the mark ULTEM resins.

Other polyimides useful in the compositions of the present invention include polyamideimides of the formulae (XIV), (XV), and (XVI) wherein n is an integer greater than about 20, preferably greater than about 50:



(XV)



Typical commercially available polyamideimides are sold under the trademark TORLON by Amoco Performance Products.

In a preferred embodiment, the composition of the present invention includes a fluoropolymer, in an amount, typically from 0.01 to 0.5 pbw fluoropolymer per 100 pbw of the thermoplastic resin composition, effective to provide anti-drip properties to the resin composition. Suitable fluoropolymers and methods for making such fluoropolymers are known, see, for example, U.S Patent Nos. 3,671,487, 3,723,373 and 3,383,092. Suitable fluoropolymers include homopolymers and copolymers that comprise structural units derived from one or more fluorinated olefin monomers. The term "fluorinated olefin monomer" means an olefin monomer that includes at least one fluorine atom substituent. Suitable fluorinated olefin monomers include, for example, fluoroethylenes such as, for example, $\text{CF}_2=\text{CF}_2$, $\text{CHF}=\text{CF}_2$, $\text{CH}_2=\text{CF}_2$, $\text{CH}_2=\text{CHF}$, $\text{CClF}=\text{CF}_2$, $\text{CCl}_2=\text{CF}_2$, $\text{CClF}=\text{CClF}$, $\text{CHF}=\text{CCl}_2$, $\text{CH}_2=\text{CClF}$, and $\text{CCl}_2=\text{CClF}$ and fluoropropylenes such as, for example, $\text{CF}_3\text{CF}=\text{CF}_2$, $\text{CF}_3\text{CF}=\text{CHF}$, $\text{CF}_3\text{CH}=\text{CF}_2$, $\text{CF}_3\text{CH}=\text{CH}_2$, $\text{CF}_3\text{CF}=\text{CHF}$, $\text{CHF}_2\text{CH}=\text{CHF}$ and $\text{CF}_3\text{CH}=\text{CH}_2$. In a preferred embodiment, the fluorinated olefin monomer is one or more of tetrafluoroethylene ($\text{CF}_2=\text{CF}_2$),

chlorotrichloroethylene ($\text{CClF}=\text{CF}_2$), vinylidene fluoride ($\text{CH}_2=\text{CF}_2$) and hexafluoropropylene ($\text{CF}_2=\text{CFCF}_3$).

Suitable fluorinated olefin homopolymers include, for example, poly(tetra-fluoroethylene), poly(hexafluoroethylene).

Suitable fluorinated olefin copolymers include copolymers comprising structural units derived from two or more fluorinated olefin copolymers such as, for example, poly(tetrafluoroethylene-hexafluoroethylene), and copolymers comprising structural units derived from one or more fluorinated monomers and one or more non-fluorinated monoethylenically unsaturated monomers that are copolymerizable with the fluorinated monomers such as, for example, poly(tetrafluoroethylene-ethylene-propylene) copolymers. Suitable non-fluorinated monoethylenically unsaturated monomers include, for example, olefin monomers such as, for example, ethylene, propylene butene, acrylate monomers such as, for example, methyl methacrylate, butyl acrylate, vinyl ethers, such as, for example, cyclohexyl vinyl ether, ethyl vinyl ether, n-butyl vinyl ether, vinyl esters such as, for example, vinyl acetate, vinyl versatate.

In a preferred embodiment, the fluoropolymer particles range in size from 50 to 500 nm, as measured by electron microscopy.

In a highly preferred embodiment, the fluoropolymer is a poly(tetrafluoroethylene) homopolymer ("PTFE").

Since direct incorporation of a fluoropolymer into a thermoplastic resin composition tends to be difficult, it is preferred that the fluoropolymer be pre-blended in some manner with a second polymer such as for, example an aromatic polycarbonate resin or a styrene-acrylonitrile resin. Methods for making suitable pre-blends are known. For example, an aqueous dispersion of fluoropolymer and a polycarbonate resin may be steam precipitated to form a

fluoropolymer concentrate for use as a drip inhibitor additive in thermoplastic resin composition, as disclosed in, for example, U.S. Patent No. 5,521,230 or, alternatively, an aqueous styrene-acrylonitrile resin emulsion or an aqueous acrylonitrile-butadiene-styrene resin emulsion and then precipitating and drying the co-coagulated fluoropolymer-thermoplastic resin composition to provide a PTFE-thermoplastic resin powder as disclosed in for example, U.S Patent No. 4,579,906.

In a preferred embodiment, the fluoropolymer additive comprises from 30 to 70 wt%, more preferably 40 to 60 wt%, of the fluoropolymer and from 30 to 70 wt%, more preferably 40 to 60 wt%, of the second polymer.

In a preferred embodiment, a fluoropolymer additive is made by emulsion polymerization of one or more monoethylenically unsaturated monomers in the presence of the aqueous fluoropolymer dispersion of the present invention to form a second polymer in the presence of the fluoropolymer. Suitable monoethylenically unsaturated monomers are disclosed above. The emulsion is then precipitated, for example, by addition of sulfuric acid. The precipitate is dewatered, for example, by centrifugation, and then dried to form a fluoropolymer additive that comprises fluoropolymer and an associated second polymer. The dry emulsion polymerized fluoropolymer additive is in the form of a free-flowing powder.

In a preferred embodiment, the monoethylenically unsaturated monomers that are emulsion polymerized to form the second polymer comprise one or more monomers selected from vinyl aromatic monomers, monoethylenically unsaturated nitrile monomer and (C₁-C₁₂)alkyl (meth)acrylate monomers. Suitable vinyl aromatic monomers, monoethylenically unsaturated nitrile monomer and (C₁-C₁₂)alkyl (meth)acrylate monomers are disclosed above.

In a highly preferred embodiment, the second polymer comprises structural units derived from styrene and acrylonitrile. More preferably, the second polymer comprises from 60 to 90 wt% structural units derived from styrene and from 10 to 40 wt% structural units derived from acrylonitrile.

The emulsion polymerization reaction mixture may optionally include emulsified or dispersed particles of a third polymer, such as, for example, an emulsified butadiene rubber latex.

The emulsion polymerization reaction is initiated using a conventional free radical initiator such as, for example, an organic peroxide compound, such as, for example, benzoyl peroxide, a persulfate compound, such as, for example, potassium persulfate, an azonitrile compound such as, for example, 2,2'-azobis-2,3,3-trimethylbutyronitrile, or a redox initiator system, such as, for example, a combination of cumene hydroperoxide, ferrous sulfate, tetrasodium pyrophosphate and a reducing sugar or sodium formaldehyde sulfoxylate.

A chain transfer agent such as, for example, a (C₉-C₁₃) alkyl mercaptan compound such as nonyl mercaptan, t-dodecyl mercaptan, may, optionally, be added to the reaction vessel during the polymerization reaction to reduce the molecular weight of the second polymer. In a preferred embodiment, no chain transfer agent is used.

In a preferred embodiment, the stabilized fluoropolymer dispersion is charged to a reaction vessel and heated with stirring. The initiator system and the one or more monoethylenically unsaturated monomers are then charged to the reaction vessel and heated to polymerize the monomers in the presence of the fluoropolymer particles of the dispersion to thereby form the second polymer.

Suitable fluoropolymer additives and emulsion polymerization methods are disclosed in EP 0 739 914 A1.

In a preferred embodiment, the second polymer exhibits a number average molecular weight of from 30,000 to 200,000 g/mol.

The thermoplastic resin composition of the present invention may optionally also contain various conventional additives, such as: antioxidants, such as, for example, organophosphites , for example, tris(nonyl-phenyl)phosphite, (2,4,6-tri-tert-butylphenyl)(2-butyl-2-ethyl-1,3-propanediol)phosphite, bis(2,4-di-t-butylphenyl)pentaerythritol diphosphite or distearyl pentaerythritol diphosphite, as well as alkylated monophenols, polyphenols, alkylated reaction products of polyphenols with dienes, such as, for example, butylated reaction products of para-cresol and dicyclopentadiene, alkylated hydroquinones, hydroxylated thiodiphenyl ethers, alkylidene-bisphenols, benzyl compounds, acylaminophenols, esters of beta-(3,5-di-tert-butyl-4-hydroxyphenol)-propionic acid with monohydric or polyhydric alcohols, esters of beta-(5-tert-butyl-4-hydroxy-3-methylphenyl)-propionic acid with monohydric or polyhydric alcohols, esters of beta-(5-tert-butyl-4-hydroxy-3-methylphenyl) propionic acid with mono-or polyhydric alcohols, esters of thioalkyl or thioaryl compounds, such as, for example, distearylthiopropionate, dilaurylthiopropionate, ditridecylthiodipropionate, amides of beta-(3,5-di-tert-butyl-4-hydroxyphenol)-propionic acid; UV absorbers and light stabilizers such as, for example, 2-(2'-hydroxyphenyl)-benzotriazoles, 2-Hydroxy-benzophenones; esters of substituted and unsubstituted benzoic acids, acrylates; fillers and reinforcing agents, such as, for example, silicates, TiO₂, glass fibers, carbon black, graphite, calcium carbonate, talc, mica; other additives such as, for example, lubricants such as , for example, pentaerythritol tetrastearate, EBS wax, silicone fluids, plasticizers, optical brighteners, pigments, dyes, colorants, flameproofing

agents; anti-static agents; blowing agents, as well as other flame retarding agents in addition to the above described organophosphorus compounds.

The invention is set forth by the following non-limiting examples and comparisons in order that it may be better understood. All United States Patents referenced herein are herewith and hereby incorporated by reference.

EXPERIMENTAL

Molding compositions were prepared by mixing together of the components in a W&P twin screw extruder with melt temperature processing range of 260 - 340 °C. Injection molded parts were obtained using Van Dorn 85 ton injection molding press.

Table 1: Formulations Tested

Formulation	1	2	3	4	5
Wt. % of Component					
PC (I)	37.697	33.000	47.322	45.947	44.572
PC (II)	30.840	27.000	38.720	37.590	36.470
ABS	5.000	20.000	6.500	6.500	6.500
PEI	20.00	3.540	0.000	2.500	5.000
FR	5.000	15.000	6.000	6.000	6.000
Lubricant	0.500	0.500	0.500	0.500	0.500
Stabilizer 1	0.300	0.300	0.300	0.300	0.300
Stabilizer 2	0.080	0.080	0.080	0.080	0.080
Stabilizer 3	0.080	0.080	0.080	0.080	0.080
Anti-Drip	0.500	0.500	0.500	0.500	0.500
Total	100.000	100.000	100.000	100.000	100.000

Notes to table 1:

- 1) BPA – bisphenol-A (BPA) Polycarbonate from GE Plastics manufactured by either an interfacial or melt process (range 60-88.5% in this study) with Mw in the range of 22000 to 29000 Daltons. Desired molecular weight of polycarbonate obtained by mixing:

PC1 - High Flow PC with Mw of 22798 Daltons

PC2 - 100 grade PC with Mw 28856 Daltons

- 2) ABS - GE Plastics Bulk ABS (range 5-20% in this study) with the following properties:

FTIR Whole Polymer	Bulk ABS 1	Bulk ABS 2
% AN	14.7	20.0
% BD	15.2	15.6
% STY	70.2	64.5
FTIR Rigid		
% AN	20.0	26.2
% STY	80.0	73.8
Rigid Mw	142000	89000
Rigid Mn	39000	31000
Rigid PD	3.6	2.9
Graft Mw	123000	55000
Graft Mn	25000	14000
Graft PD	4.9	3.9
NAVs ppm		
AN	<10	81
Sty	855	2023
EB	697	931
RPS Horiba M by Volume n	1.08	0.91

- 3) PEI - Polyetherimide - GE Plastics ULETEM 1010 (range 0-20% in this study) where T is a divlant moiety derived from bisphenol-A and R¹⁰ is a divalent meta-phenylene, i.e. a phenylene group with the two connecting valances meta to each other. The molecular weight of ULETEM 1010 is M_n (number average molecular weight) = 20,000; M_w (weight average molecular weight) = 45,000 as determined by gel permeation chromatography.

- 4) FR- Flame retardant: (range 0 – 15% in this study)
 BPA-DP flame retardant - Akzo Nobel (X4PIP and RDP could be also added in the FR description)
- 5) Lubricant – pentaerythritol tetrastearate - PETS mold release from Lonza
- 6) Stabilizer 1 - Epoxy Stabilizer from Union Carbide Corp.
- 7) Stabilizer 2 - Irganox 1076 antioxidant from Ciba Specialty Chemicals
- 8) Stabilizer 3 - Irgaphos 168 stabilizer from Ciba Specialty Chemicals
- 9) Anti- Drip -T-SAN antidrip agent - polytetrafluoroethylene encapsulated by styrene acrylonitrile from GE Plastics

Table 2: Physical Properties of Formulations

Formulation		1	2	3	4	5
Test	Units					
Notched Izod Impact	Ft-lb/in	0.6	1.5	2.6	2.1	1.6
Instru-mental Impact	Ft-lb	32	21.5	43.6	45.8	46.9
HDT	°C	108.7	79.3	103.8	105.1	105.5
Vicat (B)	°C	122	91	117.9	118	118.3
TY	Psi	10182	9227	9660	9758	89913
MVI	Cc/10 min	3.58	18.58	10.14	9.09	8.03
Spiral Flow	in	7.375	20.00	9.75	9.50	9.00

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Notes to Table 2:

- 1) Notched Izod Impact data were obtained according to ASTM D256 and measured in ft-lb/in and percent ductility at several different test temperatures;
- 2) Instrumental Impact (energy to maximal load) data were obtained according to ASTM D3763 and measured in ft-lb and percent ductility at several different test temperatures;
- 3) HDT - Heat Deflection Temperature data were measured at 264 psi on 1/4" bars according to ASTM D648;
- 4) Vicat (B) measurements were obtained according to ISO 360;
- 5) TY -Tensile Stress at Yield was obtained according to ASTM D638 using Type I 3.2 mm bars;
- 6) MVI (Melt Volume Index) data were obtained according to ASTM D1238 at 260 °C and 2.16 kg load and measured in cc/min;
- 7) Spiral Flow Length was measured in inches at 2.3 mm spiral thickness using the following conditions - 470 °F melt temperature; 1500 psi fill pressure and 6 sec. injection time.

Table 3: Flammability Test Data

Test	Bar Thick-ness	1	2	3	4	5
5VB Pass/Fail	3 mm	P	P	F	P	P
	2.5 mm	P	P	F	P	P
	2.3 mm	P	P	F	F	F
	2 mm	P	P	F	F	F
	1.8 mm	F	P	F	F	F
UL94V0 min. rating - 20 bars	2 mm	V0	V0	V0	V0	V0
	1.8 mm	V0	V0	V1	V0	V0
	1.5 mm	V1	V0	FAIL	V1	V1
Average FOT - 20 bars	2 mm	2.7	1.7	4.7	2.3	2.4
	1.8 mm	6.8	2	7.1	3.8	3.5
	1.5 mm	8.1	3.1	15	10.7	13.3

Discussion

Surprisingly addition of small amounts of polyetherimide resin to the flame retardant PC/ ABS blend 3 at 2.5% and 5% levels (Blends 4 and 5) results in the following flame performance improvement versus the control blend 3 (Table 3):

- 1) 5VB pass at 3.0 and 2.5 mm (the control blend fails at these thicknesses);
- 2) V0 ratings at 1.8 for blends 4 and 5 where the control blend 3 tests V1;
- 3) V1 ratings for blends 4 and 5 at 1.5 mm where the control blend 3 tests "Fail"; and
- 4) Reduced average Flameout time (FOT) in the UL94V0 test based on 20 bars burn.

Thus for example at 1.8 mm the control blend 3 FOT is 7.1 sec while the blends with added 2.5% and 5% Ultem - 4 and 5 exhibit FOT's at 3.8 and 3.5 sec. respectively. In the same series of comparative blends - control blend 3 with no polyetherimide and blends 4 and 5 derived from blend 3 via addition of 2.5% and 5% of polyetherimide, the following changes of physical properties occur (Table 2):

- 1) Slight increase in the Heat Deflection Temperature with 1.3 to 1.7 °C for blends 4 and 5 versus the control blend 3 mirrored by a similar but smaller magnitude shift in the Vicat B measurement (0.2 to 0.4 degrees C increase);
- 2) Increase of Dynatup impact energy with 2.2 and 3.3 ft-lb for blends 4 and 5 versus the control blend 3 while an opposite trend is observed for the Notched Izod Impact which decreases with 0.5 and 1 ft-lb/in for blends 4 and 5 versus the control blend 3 respectively;
- 3) Increased tensile stress at yield with 98 and 253 psi for blends 4 and 5 versus the control 3; and
- 4) Blends 4 and 5 exhibit also slightly lower flow versus the control 3 as measured by both MVI as well as Spiral flow.

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